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AIR QUALITY

MARATHON

Annual Report, 1977

TECHNICAL SUPPORT SECTION
NORTHWESTERN REGION
ONTARIO MINISTRY OF THE ENVIRONMENT

May, 1978

CONTENTS

SUMMARY

The Ontario Ministry of the Environment has conducted air quality assessment investigations in Marathon since 1974. This report presents results of the 1977 programme, which included vegetation and soil studies and air quality monitoring in the vicinity of a kraft pulp mill and adjacent chlor-alkali plant.

Further information was obtained on mercury contamination of soil in a small area some distance from the mill. Although very high mercury concentrations were found in surface soil at the site investigated, the pollution source was not established.

As in 1976, surface water run-off from the hillside adjacent to the mill was low in mercury. This finding suggests that little mercury is being lost to run-off water from this localized area of severely contaminated soil.

In contrast to 1975 and 1976, there was no evidence of sulphur dioxide injury to local vegetation.

A moss bag exposure experiment confirmed that airborne calcium, chloride, mercury and sodium were present at elevated concentrations downwind of the mill, thereby indicating the latter as the source of emissions.

Although dustfall was often above Ontario air quality objectives, a number of the high readings were attributed to sources other than emissions from the mill. Sulphation rate measurements indicated that concentrations of total reduced sulphur and sulphur dioxide were periodically above acceptable levels near the kraft mill.

INTRODUCTION

Since 1974, the Ontario Ministry of the Environment has conducted an air quality assessment programme in the vicinity of a 500 ton-per-day bleached kraft pulp mill in the town of Marathon. Earlier investigations (1, 2) reported results from vegetation and soil assessment surveys, moss bag exposure experiments, snow sampling, and air quality monitoring. The Ministry's 1977 programme included a continuation of some aspects of the vegetation and soil studies, and the exposure of another set of moss bags. Because of possible interferences from construction activity near the pulp mill, no snow sampling was conducted. Measurement of dustfall and sulphation was continued in 1977 at five locations near the mill and in the adjacent town area, and at one site in Heron Bay. The Ministry's Air Resources Branch also undertook a brief air quality survey in late 1977 using mobile monitoring equipment. Results of this study will appear in a separate report.

VEGETATION AND SOIL ASSESSMENT

SOIL AND SOIL DRAINAGE-WATER

Soil

Soil samples from surveys in 1975 and 1976 demonstrated the presence of very high mercury concentrations in surface soil near the pulp mill and adjacent mercury-cell chlor-alkali plant. Atmospheric emissions from the latter were judged to be responsible for the observed contamination. Two, apparently unrelated, local areas of mercury contamination of soil were also discovered: one near a warehouse where mercury-laden waste was temporarily stored, and another location about 625 m (metres) south of the pulp mill.

At the latter site, a nine-point sampling survey failed to establish the extent of contamination. A further set of samples, from 21 points, was therefore obtained in June, 1977.

Soil was collected with a stainless steel corer, 2.5 cm (centimetres) in outside diameter. Surface debris and loose organic matter were removed from the ground surface before each insertion of the corer. At least 10 cores of soil, to a depth of 5 cm, were pooled to form one sample, which was placed in a polyethylene bag to await processing. Triplicate samples were obtained from each site. At the Ministry's Thunder Bay laboratory, collected material was spread on paper and air-dried for 48 hours, coarse screened to remove stones and organic matter, then fine screened through an 80-mesh sieve. Processed soil was submitted to the Ministry's central laboratory in Toronto for mercury analysis. About 0.2 g of soil from each sample was digested in mixed acids at low temperature, then subjected to ultraviolet atomic absorption to determine mercury content.

The mercury concentrations reported for the study area are plotted in Figure 1. Mercury at both control sites was well below the Ministry guideline of 0.3 µg/g (micrograms per gram, dry weight). Mercury levels at the bottom of two, shallow, man-made excavations in the survey area, were at or below 1 µg/g, indicating that these holes were not centres of contamination. The data in Figure 1 show that further sampling will be required to fully define the area affected. The source of contamination has not been determined, but flooding from the effluent ditch is a possibility under consideration.

Soil Drainage-Water

Surface run-off water was collected in late March and mid-August from five locations near the chemical plant (Figure 2). Each sample, approximately 100 ml (millilitres) in volume, was collected in a clean, plastic-capped, glass bottle, preserved with one drop of saturated potassium permanganate solution and 1 ml concentrated nitric acid, then submitted to the Ministry's Thunder Bay laboratory for mercury analysis by ultraviolet atomic absorption.

Drainage-water mercury concentrations are reported in Table 1. Values were of the same order of magnitude as those documented in 1976(1), thereby strengthening the tentative conclusion that surface water run-off is not a mechanism of significant mercury loss from contaminated soil near the mill.

VEGETATION INJURY

All vegetation around the mill was inspected twice during the 1977 growing season (June 29 and August 19). Evidence of injury, caused by several disease organisms, was noted on foliage of common species of trees and shrubs, but there were no visible symptoms of air pollution damage. During the past four years, vegetation injury attributed to sulphur dioxide was observed in 1975 and 1976, but not in 1974 or 1977. When occurring, sulphur dioxide injury was restricted to small areas near the mill and was never found in the town area.

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MOSS BAG EXPOSURE

Mosses are effective substrates for absorbing and retaining some types of airborne contaminants by a passive ion-exchange process. Techniques have been developed to suspend small quantities of moss in mesh bags at strategic locations to monitor the atmospheric environment(3). At Marathon, bags of *Sphagnum* moss were exposed from June 29 to August 19 at 24 sites (Figure 2) plus two controls. The 1977 monitoring locations were the same as those used in 1976, except for the deletion of three sites (1, 26 and 27) and the relocation of sites 12 and 17 because of local construction activity. Each sample comprised about 4 g (grams) of oven-dried moss contained in a 10 by 20 cm envelope of fibreglass screening attached with Velcro strips to a supporting structure about 2.5 m above ground level. Samples, after exposure, were placed in polyethylene bags for refrigerated storage ($4^{o}C$) until processed at the Ministry's Thunder Bay laboratory. The moss was dried at $80^{o}C$ for 30 hours, then ground in a Wiley mill equipped with a 1-mm pore-size screen. Mercury analysis, at the Ministry's Toronto laboratory, was carried out by the same procedure outlined for soil. Chloride was determined colorimetrically, and calcium and sodium were analysed by atomic absorption spectrophotometry after the moss was ashed at high temperature.

The analytical data are summarized in Table 2 and plotted in Figures 3a to 3d. Results for the 1977 exposure trial were very similar to those for 1976. A pronounced gradient of decreasing concentrations with increasing distance from the mill was noted for all elements. Elevated chloride was also found to the northwest of the brine chests, near a salt conveyor belt. Distribution patterns of all contaminants reflected the strong influence of local topography and prevailing winds. Further exposure experiments are scheduled in 1978 to assess changes in airborne mercury following closure of the chlor-alkali plant in August, 1977.

AIR MONITORING

PARTICULATE POLLUTANTS

Dustfall

Dustfall, one of the most visible classes of air pollutants, comprises particulate matter which settles out from the atmosphere under the influence of gravity. It is measured by exposing open-top plastic jars to the air for 30 days and weighing the collected matter. Specific components of dustfall, such as sulphate and heavy metals, may be determined analytically, and other constituents, such as wood fibres, pollen and grain dust, may be identified microscopically. Results are normally expressed in g/m^2 (grams per square metre) for 30 days. The Ontario air quality objectives for total dustfall are 7 g/m^2 for 30 days and 4.6 g/m^2, annual average. These values are equivalent to 20 and 30 tons per square mile which were, respectively, the monthly and annual objectives before conversion to metric units in January, 1977.

The 1977 monitoring sites are shown in Figure 4, and dustfall results are summarized in Table 3. Average dustfall was higher in 1977 than in 1975 or 1976, and exceeded the annual objective at all sites. Soluble sulphate accounted for about 10 percent of total dustfall at all locations except at station 63027, closest to the mill, where sulphate constituted about 14 percent of dustfall. Many of the high dustfall levels were not attributed to mill emissions. For example, most dustfall at site 63028 was probably from dust blown from a nearby parking area. Relocation of this station is under consideration.

GASEOUS POLLUTANTS

Sulphation Rates

Sulphation rates provide an indication of the presence of undesirable sulphur-containing gases in the air. They are determined by exposing small plastic dishes, coated with lead dioxide, to the atmosphere for 30-day periods. Lead dioxide reacts with gaseous sulphur compounds to form lead sulphate. The amount of sulphate formed is determined analytically and reported as mg SO_3/100 cm^2/day (milligrams of sulphur trioxide per hundred square centimetres per day). In addition to sulphur dioxide, reactive gases such as hydrogen sulphide and other organic sulphides also convert lead dioxide to the sulphate form. In Marathon, where all these compounds are present at measurable levels, the coated plates therefore yield results representing the composite effect of several pollutants.

Table 3 gives the 1977 sulphation rate data for monitoring sites shown in Figure 4. Values for 1977 were similar to those for 1976. Highest averages were at sites closest to the mill (Figure 5). Although sulphation rates at station 63031 exceeded the Ontario air quality objective of 0.70 mg SO_3/100 cm^2/day in three months of the year, the objective is of questionable value where mixtures of reactive pollutants occur. The data indicate that concentrations of sulphur-containing gases are periodically well above background levels close to the mill. This conclusion is supported by results of a 1976 mobile monitoring survey, which showed that sulphur dioxide and total reduced sulphur frequently exceeded provincial standards in the vicinity of the mill. Sulphation rates at Heron Bay were above background levels but were not considered excessive.

REFERENCES

1. Ontario Ministry of the Environment. 1977. Air quality, Marathon. Annual Report, 1976.

2. Griffin, H. D. 1976. Air quality, Marathon. Annual Report, 1975.

3. Goodman, G. T. and T. M. Roberts. 1971. Plants and soils as indicators of metals in the air. Nature 231:287-292.

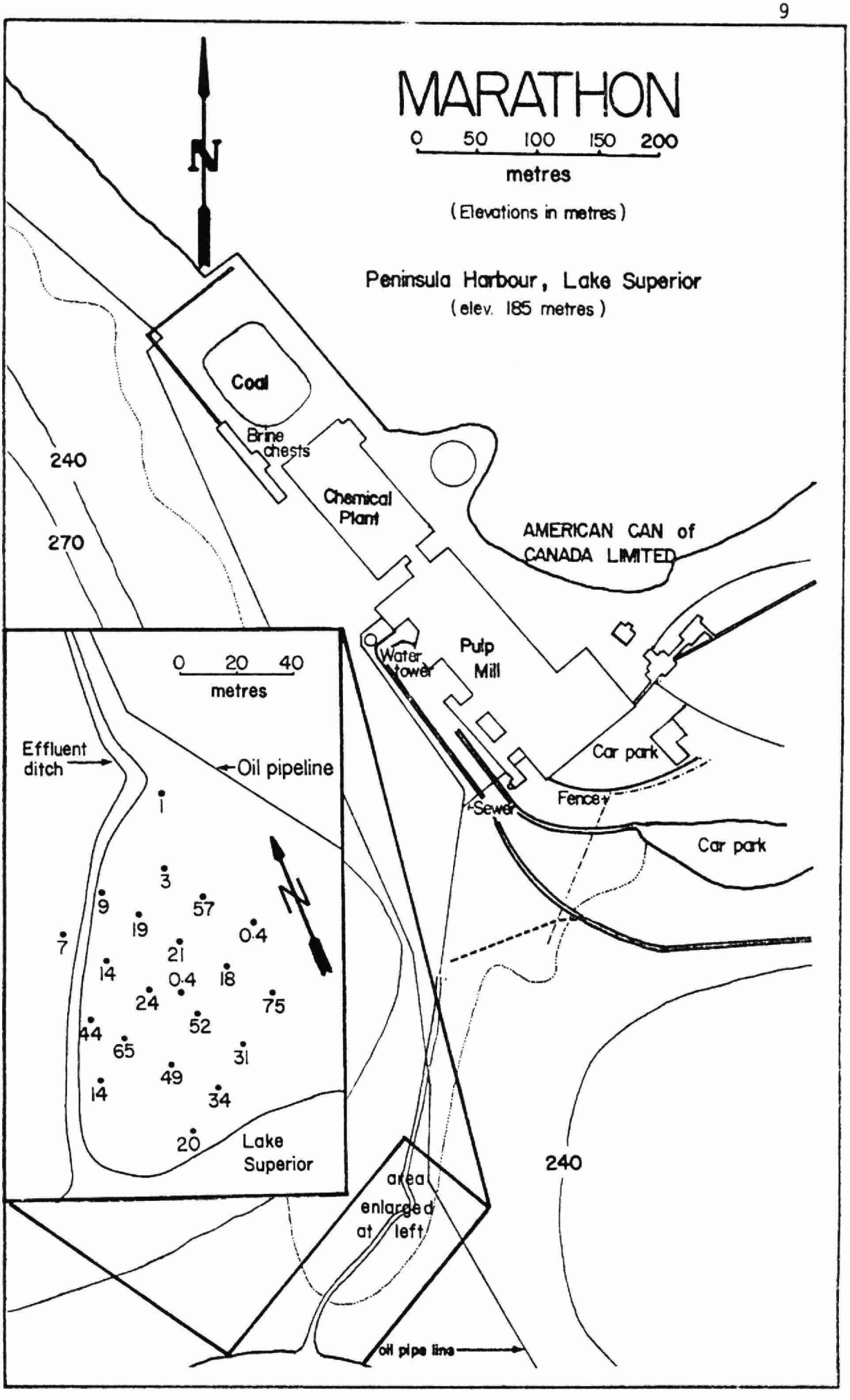

Figure 1. Mercury concentrations (µg/g, dry weight) in surface soil (0-5 cm), June, 1977.

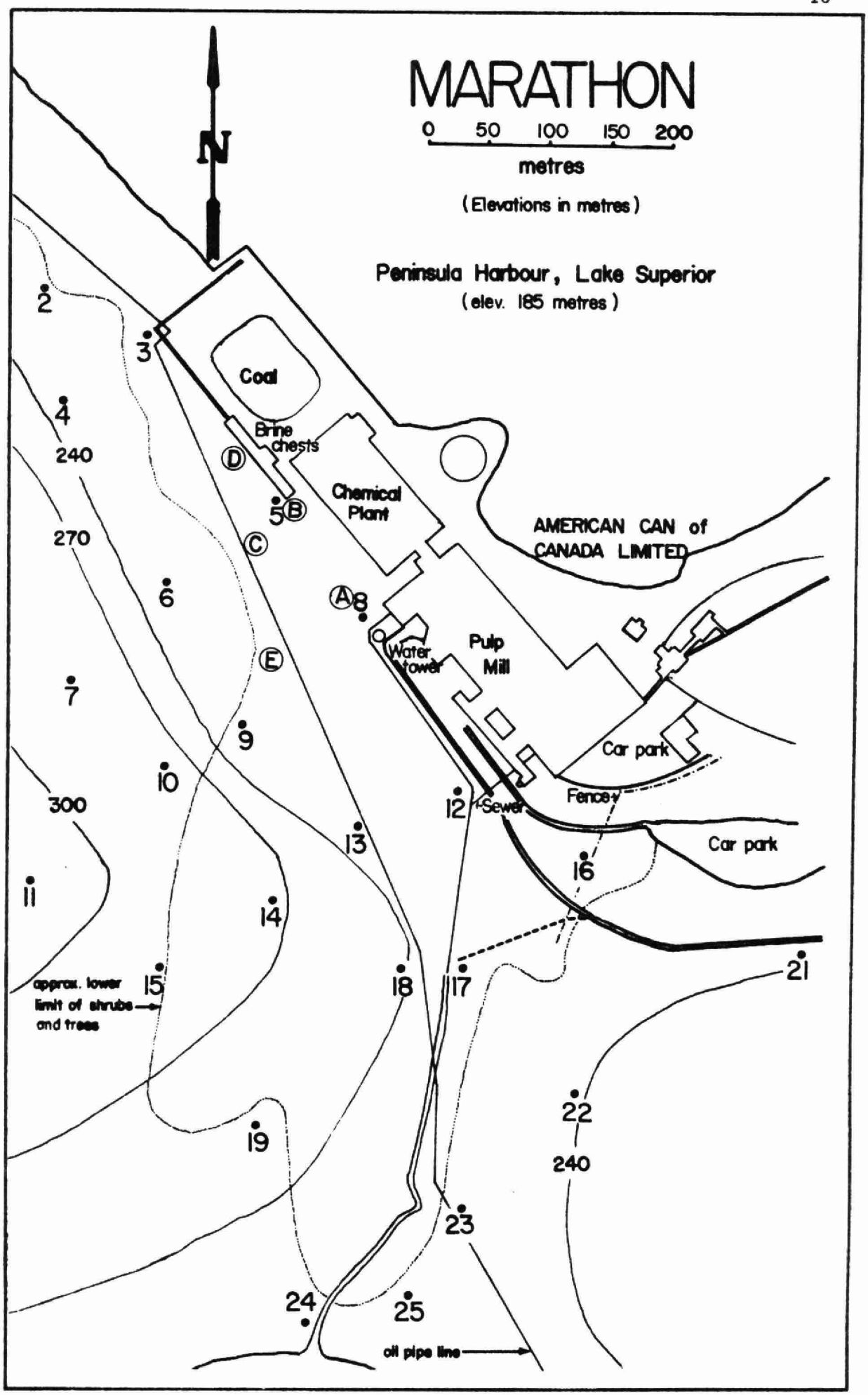

Figure 2. Moss exposure sites (2-25) and soil drainage-water sampling sites (A-E), 1977.

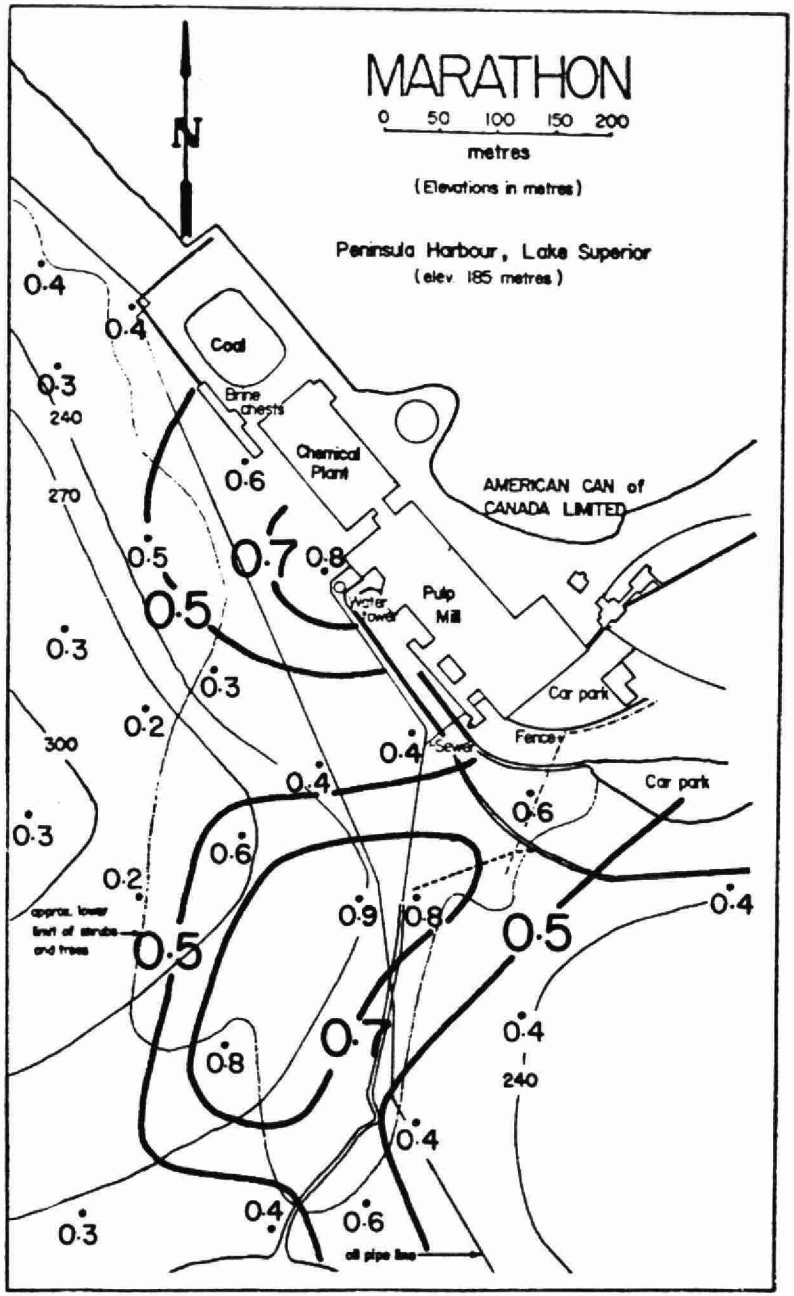

Figure 3a. Calcium levels (%, dry weight) in moss exposed June 29 to August 19, 1977.

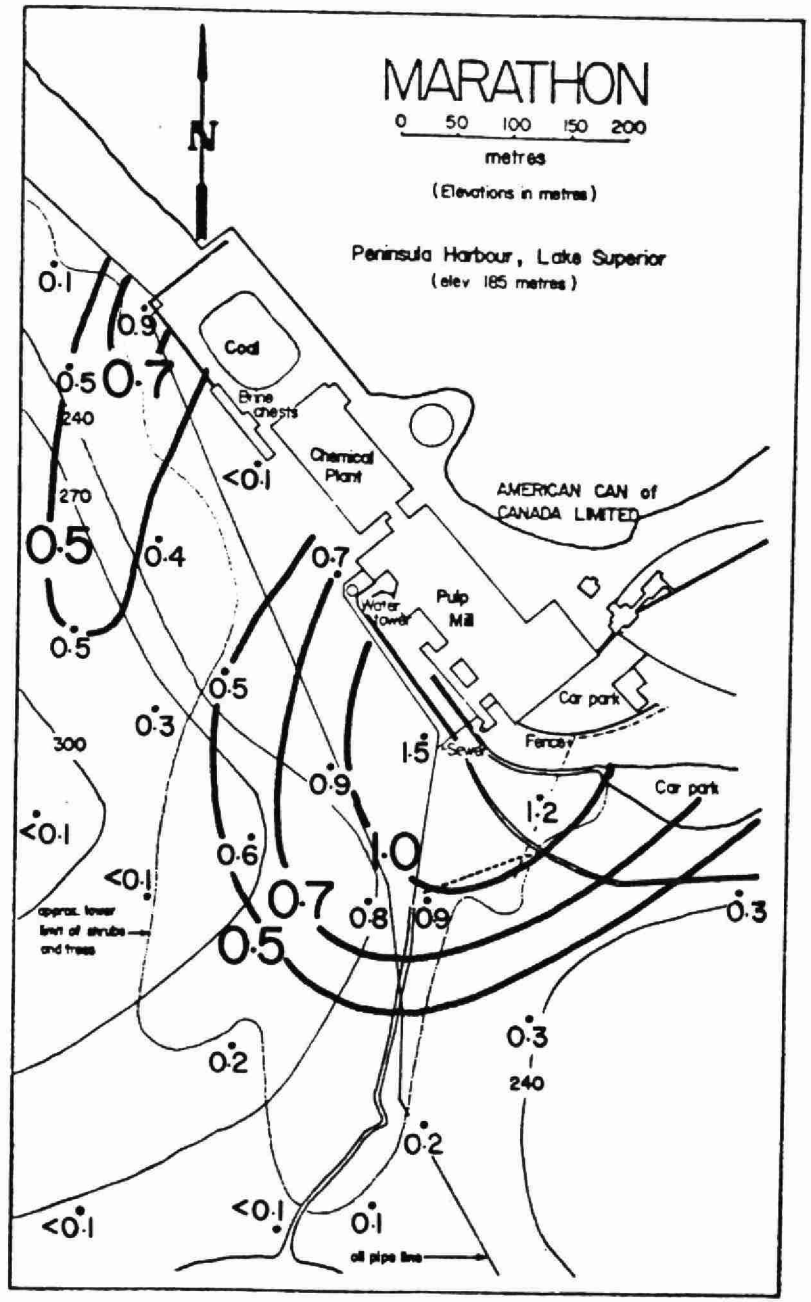

Figure 3b. Chloride levels (%, dry weight) in moss exposed June 29 to August 19, 1977.

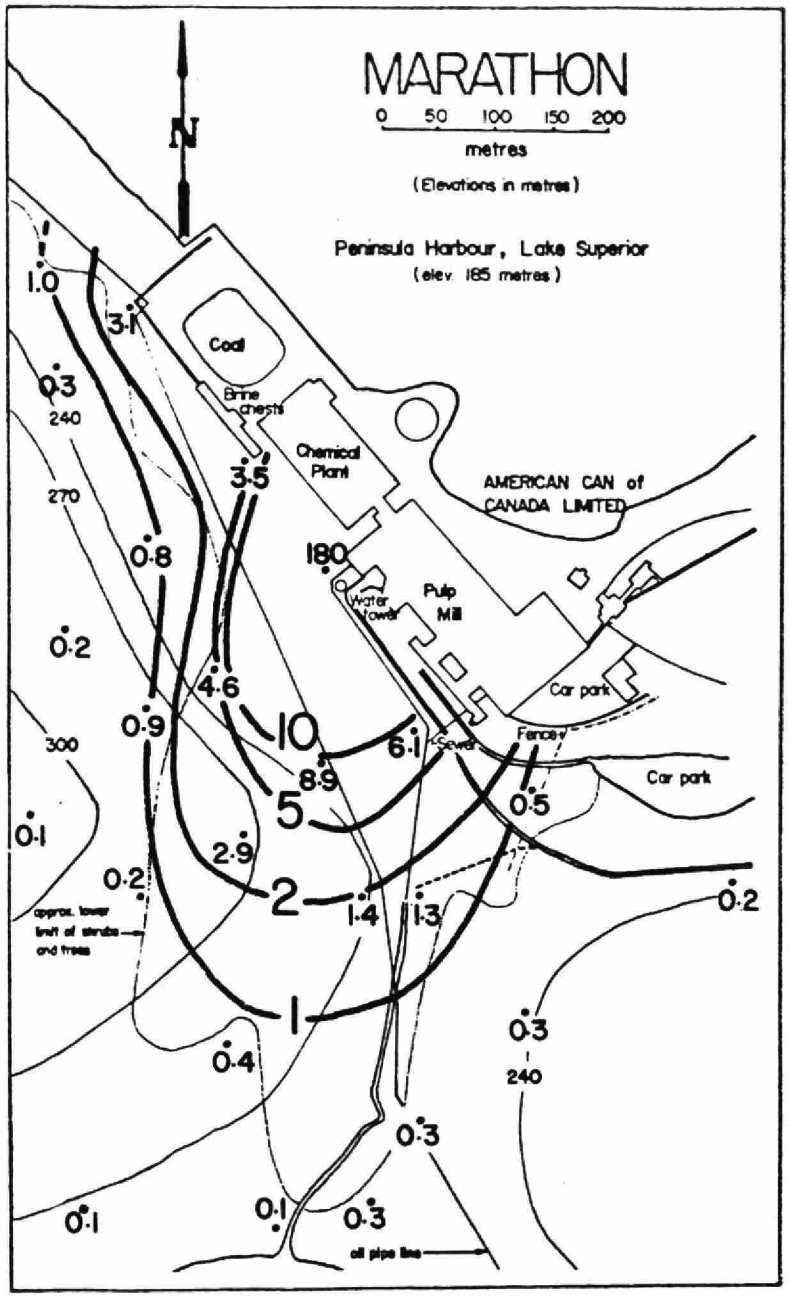

Figure 3c. Mercury levels (µg/g, dry weight) in moss exposed June 29 to August 19, 1977.

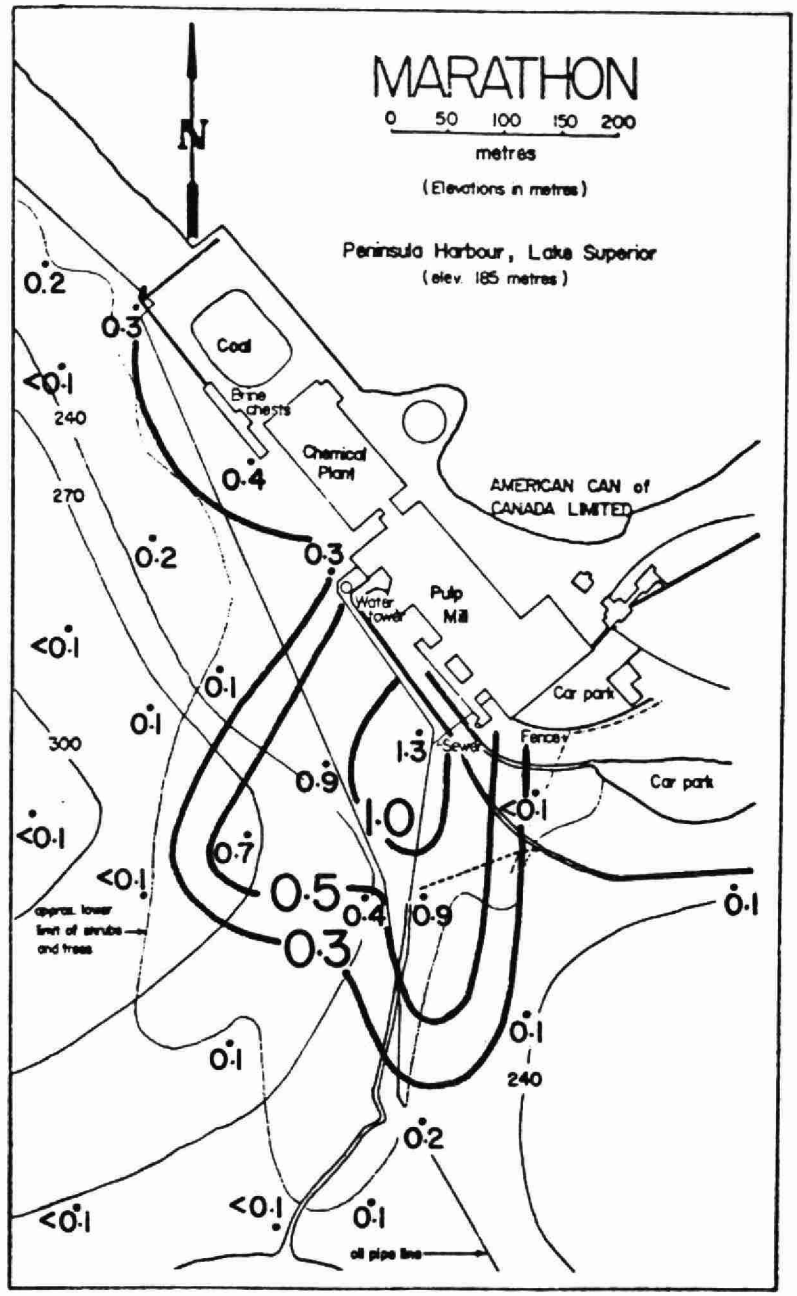

Figure 3d. Sodium levels (%, dry weight) in moss exposed June 29 to August 19, 1977.

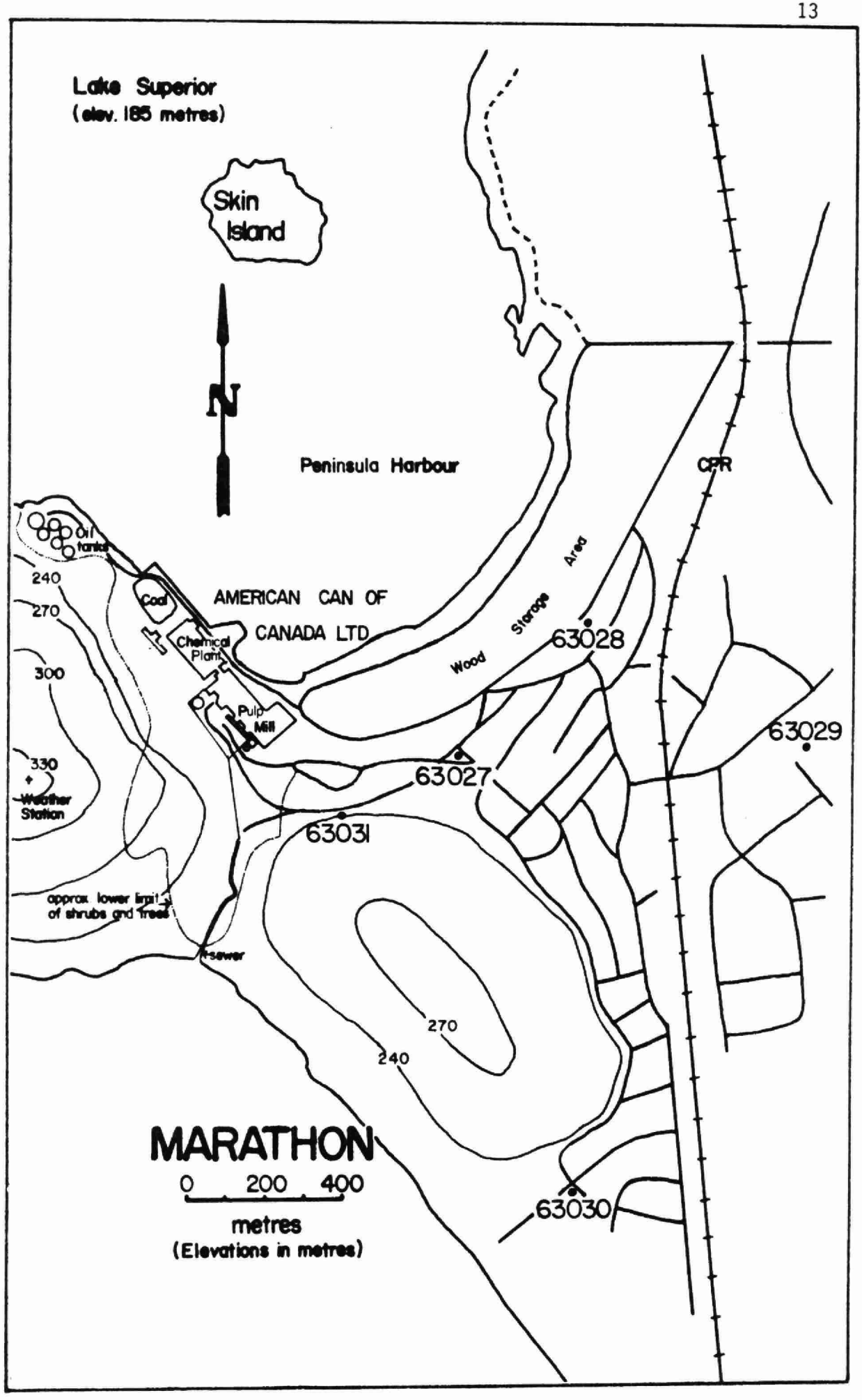

Figure 4. Air quality monitoring sites, 1977 (except station 63032, Heron Bay).

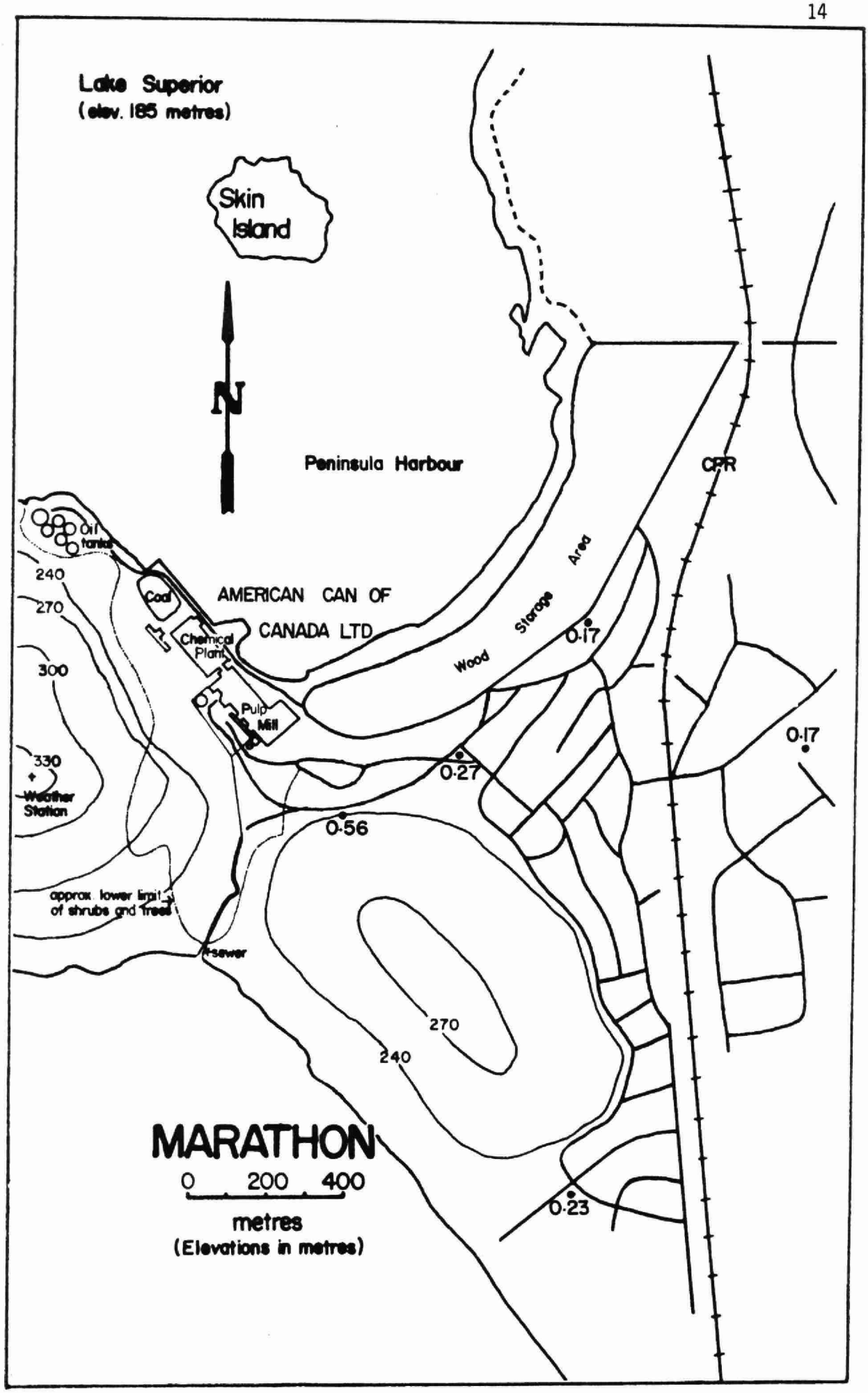

Figure 5. Average sulphation rates, 1977 (mg SO_3 / 100 cm^2 / day).

TABLE 1. Mercury concentrations (µg/l) in surface run-off water near American Can chemical plant, Marathon, 1977.

Location	Date of sampling	Mercury concentration
A	March 29	1.6
B	March 29	1.6
	August 19	13.2
C	March 29	0.8
D	August 19	<1.0
E	August 19	<1.0

TABLE 2. Concentrations, dry weight basis, of calcium, chloride, mercury and sodium in moss exposed June 29 to August 19, 1977.

Site	Calcium (%)	Chloride (%)	Mercury (µg/g)	Sodium (%)
2	0.4	0.1	1.0	0.2
3	0.4	0.9	3.1	0.3
4	0.3	0.5	0.3	<0.1
5	0.6	<0.1	3.5	0.4
6	0.5	0.4	0.8	0.2
7	0.3	0.5	0.2	<0.1
8	0.8	0.7	180	0.3
9	0.3	0.5	4.6	0.1
10	0.3	0.3	0.9	0.1
11	0.3	<0.1	6.1	<0.1
12	0.4	1.5	8.9	1.3
13	0.4	0.9	2.9	0.9
14	0.6	0.6	0.2	0.7
15	0.2	<0.1	0.5	<0.1
16	0.6	1.2	1.3	<0.1
17	0.8	0.9	1.4	0.9
18	0.9	0.8	0.4	0.4
19	0.8	0.2	0.1	0.1
20	0.3	<0.1	0.2	<0.1
21	0.4	0.3	0.2	0.1
22	0.4	0.3	0.3	0.1
23	0.4	0.2	0.1	0.2
24	0.4	<0.1	0.3	<0.1
25	0.6	0.1	0.1	0.1
Exp.[a] control	0.2	<0.1	<0.1	<0.1
Exp. control	0.3	<0.1	<0.1	<0.1
Unexp.[b] control	0.3	<0.1	<0.1	<0.1
Unexp. control	0.3	<0.1	<0.1	<0.1

[a]Exposed

[b]Unexposed

TABLE 3. Total dustfall, sulphate in dustfall and sulphation rates, Marathon, 1977.

Station	Location	Distance (metres) and direction from source[a]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
			Dustfall (g/m^2/30 days)												
63027	McLeod/Abrams	590 ESE	3.1	1.3	7.5[b]	6.8	6.8	17.6	12.8	10.9	8.1	2.1	4.2	-	7.4
63028	Winton/Stevens	875 E	2.8	0.7	18.4	14.5	15.0	18.6	12.1	11.8	7.2	11.2	6.3	-	10.8
63029	Marathon Shell	1390 E	1.9	0.7	7.8	4.7	4.7	5.0	6.9	10.4	6.1	3.6	25.7	-	7.0
63030	Howe/Yawkey	1390 SE	2.2	3.6	6.4	5.9	6.2	13.1	9.9	5.0	3.8	1.1	7.0	-	5.8
			Soluble sulphate in dustfall (g/m^2/30 days)												
63027	McLeod/Abrams	590 ESE	0.6	0.4	1.5	1.0	0.8	1.9	1.8	2.2	0.5	0.7	0.4	0.5	1.0
63028	Winton/Stevens	875 E	0.4	0.2	2.3	2.4	1.2	1.8	1.6	1.7	0.6	1.1	0.5	0.1	1.2
63029	Marathon Shell	1390 E	0.4	0.2	0.7	0.6	0.5	0.8	1.0	1.1	0.5	0.5	0.6	0.2	0.6
63030	Howe/Yawkey	1390 SE	0.3	0.5	0.6	0.3	0.4	0.9	0.8	0.7	0.4	0.3	0.3	0.2	0.5
			Sulphation rate (mg SO_3/100 cm^2/day)												
63027	McLeod/Abrams	590 ESE	.18	.13	.38	.13	.20	-	.30	.28	.16	.19	.31	.49	.27
63028	Winton/Stevens	875 E	.09	.06	.14	.13	.12	.20	.26	.31	.13	.15	.26	.14	.17
63029	Marathon Shell	1390 E	.14	.12	.33	.13	.13	.14	.21	.19	.13	.15	.16	.24	.17
63030	Howe/Yawkey	1390 SE	.27	.31	.25	.13	.20	-	.35	.09	.13	.19	.26	.36	.23
63031	Bark Press Road	420 SE	.32	1.21	.55	.13	.42	.20	1.23	.40	.15	.75	.69	.73	.56
63032	Heron Bay	14000 SE								.01	.12	.14	.13	.17	

[b]Values above objectives of 7.0 (monthly) or 4.6 (annual average) are underlined.

[a]Source arbitrarily designated as recovery furnace stacks, American Can of Canada Limited kraft pulp mill.

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